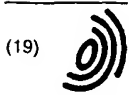


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(54) Fuel compositions with enhanced combustion characteristics

Kraftstoffzusammensetzungen mit erhöhten Verbrennungseigenschaften

Compositions de combustible à caractéristiques de combustion augmentées

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• Henly, Timothy James
St. Louis, Missouri 63119 (US)

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(74) Representative: Woods, Geoffrey Corlett et al
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

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(73) Proprietor: ETHYL PETROLEUM ADDITIVES,
INC.
Richmond, Virginia 23219-4304 (US)

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(72) Inventors:
• Cunningham, Lawrence Joseph
Kirkwood, Missouri 63122 (US)
• Kulnowski, Alexander Michael
St. Louis, Missouri 63125 (US)

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Description

This invention relates to preservation of the environment. More particularly, this invention relates to fuel compositions and methods that reduce atmospheric pollution normally caused by the operation of engines or combustion apparatus on middle distillate fuels.

The importance and desirability of reducing the release of pollutants into the atmosphere are well recognized. Among the pollutants sought to be reduced are nitrogen oxides (NO_x), carbon monoxide, unburned hydrocarbons, and particulates.

French Patent Specification 821211 describes motor fuels, especially diesel fuels, containing a combustion accelerator, in particular a mixture of dissolved aryl nitrates, to increase the cetane number of the fuel.

This invention involves the discovery, inter alia, that it is possible to reduce the amount of NO_x or CO or unburned hydrocarbons released into the atmosphere during operation of engines or other combustion apparatus operated on middle distillate fuel by employing as the fuel a middle distillate fuel having a sulfur content of 500 ppm or less and having dissolved there in a combustion improving amount of at least one organic nitrate combustion improver consisting essentially of 2-ethylhexyl nitrate. In fact it has been found possible through use of such fuel compositions to reduce the amount of two and in some cases all three such pollutants (NO_x , CO and unburned hydrocarbons) emitted by diesel engines. Moreover this important and highly desirable objective has been and thus may be achieved without suffering an undesirable increase in the emission of particulates. This is a unique discovery since the available experimental evidence and mechanistic theories of combustion suggest that if NO_x is reduced, the amount of particulates will be increased, and vice versa.

Accordingly this invention provides the use of at least one fuel-soluble combustion improver consisting essentially of 2-ethylhexyl nitrate, incorporated in a hydrocarbonaceous middle distillate fuel having a sulfur content of less than 500 ppm prior to combustion in a proportion of 1000 to 5000 parts by weight per million parts of fuel for reducing emissions of at least two of NO_x , CO and unburned hydrocarbons during combustion of said fuel, having the distillation profile disclosed in claim 1 and page 6, in a diesel engine in the presence of air.

The hydrocarbonaceous middle distillate fuel preferably has a sulfur content of 100 ppm or less and most preferably no more than 60 ppm. By the term "hydrocarbonaceous" as used in the ensuing description and appended claims is meant the middle distillate fuel is composed principally or entirely of fuels derived from petroleum by any of the usual processing operations. The finished fuels may contain, in addition, minor amounts of non-hydrocarbonaceous fuels or blending components such as alcohols, dialkyl ethers, or like materials, and/or minor amounts of suitably desulfurized auxiliary liquid fuels of appropriate boiling ranges (i.e. between about 160 and about 370°C) derived from tar sands, shale oil or coal. When using blends composed of such desulfurized auxiliary liquid fuels and hydrocarbonaceous middle distillate fuels, the sulfur content of the total blend must be kept below 500 ppm.

This invention thus provides improvements in the operation of motor vehicles and aircraft which operate on middle distillate fuels. These improvements involve fuelling the vehicle or aircraft with a hydrocarbonaceous middle distillate fuel having a sulfur content of less than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and containing the aforesaid organic nitrate combustion improver dissolved therein.

In accordance with a particularly preferred embodiment of this invention, there is provided the use of a hydrocarbonaceous middle distillate fuel having a sulfur content of not more than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and a 10% boiling point (ASTM D-86) in the range of about 154° to about 230°C, said fuel containing a minor combustion improving amount of at least one fuel-soluble organic nitrate combustion improver consisting essentially of 2-ethylhexyl nitrate. Such fuel compositions tend on combustion to emit especially low levels of NO_x . Without desiring to be bound by theoretical considerations, one explanation for such highly desirable performance is that fuels with higher 10% boiling points cause a delay in the progression of combustion and consequent higher peak temperatures which increase the amount of NO_x formation.

Pursuant to another particularly preferred embodiment of this invention there is provided the use of a hydrocarbonaceous middle distillate fuel having a sulfur content of not more than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and a 90% boiling point (ASTM D-86) in the range of about 260° to about 320°C, said fuel containing a minor combustion improving amount of at least one fuel-soluble organic nitrate combustion improver consisting essentially of 2-ethylhexyl nitrate. Such fuel compositions tend on combustion to emit especially low levels of particulates.

These and other embodiments are set forth in the ensuing description and appended claims.

In the accompanying drawings:

Fig. 1 is a least-squares plot of NO_x emissions versus 10% boiling temperatures of fuels having a nominal cetane number of approximately 50; and

Fig. 2 is a least-squares plot of particulate emissions versus 90% boiling temperatures of fuels having a nominal cetane number of approximately 50.

The hydrocarbonaceous fuels utilized in the practice of this invention are comprised in general of mixtures of hydrocarbons which fall within the distillation range of about 160 to about 370°C. Such fuels are frequently referred to as "middle distillate fuels" since they comprise the fractions which distill after gasoline. Such fuels include diesel fuels, burner fuels, kerosenes, gas oils, jet fuels, and gas turbine engine fuels.

The used middle distillate fuels are those characterized by having the following distillation profile.

	°F	°C
IBP	250 - 500	121 - 260
10%	310 - 550	154 - 288
50%	350 - 600	177 - 316
90%	400 - 700	204 - 371
EP	450 - 750	232 - 399

Diesel fuels having a clear cetane number (i.e., a cetane number when devoid of any cetane improver such as an organic nitrate) in the range of 30 to 60 are preferred. Particularly preferred are those in which the clear cetane number is in the range of 40 to 50.

The organic nitrate combustion improvers (also frequently known as ignition improvers) comprise nitrate esters of substituted or unsubstituted aliphatic or cycloaliphatic alcohols which may be monohydric or polyhydric. Preferred organic nitrates are substituted or unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, preferably from 2 to 10 carbon atoms. The alkyl group may be either linear or branched (or a mixture of linear and branched alkyl groups). Specific examples of nitrate compounds suitable for use as nitrate combustion improvers include, but are not limited to, the following: methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, n-heptyl nitrate, sec-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, isopropylcyclohexyl nitrate, and the like. Also suitable are the nitrate esters of alkoxy substituted aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxy)ethyl nitrate, 1-methoxypropyl-2-nitrate, and 4-ethoxybutyl nitrate, as well as diol nitrates such as 1,6-hexamethylene dinitrate, and the like. Preferred are the alkyl nitrates having from 5 to 10 carbon atoms, most especially mixtures of primary amyl nitrates, mixtures of primary hexyl nitrates, and octyl nitrates such as 2-ethylhexyl nitrate.

As is well known, nitrate esters are usually prepared by the mixed acid nitration of the appropriate alcohol or diol. Mixtures of nitric and sulfuric acids are generally used for this purpose. Another way of making nitrate esters involves reacting an alkyl or cycloalkyl halide with silver nitrate.

The concentration of nitrate ester in the fuel can be varied within relatively wide limits such that the amount employed is at least sufficient to cause a reduction in emissions. This amount falls within the range of 1,000 to 5,000 parts by weight per million parts of fuel.

Other additives may be included within the fuel compositions of this invention provided they do not adversely affect the exhaust emission reductions achievable by the practice of this invention. Thus use may be made of such components as organic peroxides and hydroperoxides, corrosion inhibitors, antioxidants, antirust agents, detergents and dispersants, friction reducing agents, demulsifiers, dyes, inert diluents, and like materials.

The advantages achievable by the practice of this invention were demonstrated in a sequential series of engine tests in which a Detroit Diesel 11.1 liter Series 60 engine mounted to an engine dynamometer was used. The system was operated on the "EPA Engine Dynamometer Schedule for Heavy-Duty Diesel Engines" set forth at pages 810-819 of Volume 40, Part 86, Appendix I, of the Code of Federal Regulations (7-1-86). In these tests, the first of five consecutive tests involved operation of the engine on a conventional DF-2 diesel fuel having a nominal sulfur content in the range of 2000 to 4000 ppm. This test served as one of two baselines. In the next operation the engine was run using a low-sulfur diesel fuel having the following characteristics:

Sulfur, ppm	50
Gravity, API @ 60°F (15.5°C)	34.7
Pour Point, °F (°C)	- 5 (-20)
Cloud Point, °F (°C)	8 (-13)
Copper Strip	1
Distillation, °F (°C)	
IBP	332 (167)

Continuation of the Table on the next page

(continued)

10%	430 (221)
50%	532 (278)
90%	632 (333)
EP	634 (334)
Cetane Number	44.3
Viscosity @ 40°C, cS	2.96

In the third and fourth tests -- which represented the practice of this invention -- this same low-sulfur fuel was used except that it had blended therein a diesel ignition improver composed of 2-ethylhexyl nitrate. In the third test the concentration was 2000 ppm of the organic nitrate. In the fourth test, the fuel contained 5000 ppm of the organic nitrate. The fifth and final test involved another baseline run using the initial conventional DF-2 diesel fuel. In all instances the quantities of NO_x, unburned hydrocarbons ("HC"), carbon monoxide ("CO") and particulates emitted by the engine were measured and integrated. The results of these tests are summarized in the following table. The values shown therein for NO_x, HC, CO, and Particulates, are presented in terms of grams per brake horsepower per hour (i.e. grams per 745 watts per hour). Thus the lower the value, the lower the rate and amount of emissions.

Test No.	NO _x	HC	CO	Particulates
1	4.641	0.086	1.414	0.227
2	4.345	0.068	1.490	0.165
3	4.173	0.051	1.312	0.164
4	4.208	0.073	1.324	0.165
5	4.623	0.078	1.525	0.223

In particularly preferred embodiments of this invention, use of fuels having certain boiling characteristics as well as low sulfur levels, results in still further reductions in either NO_x or particulate emissions. Thus by use of fuels meeting the low sulfur parameters set forth hereinabove and additionally having a 10% boiling point (ASTM D-86) in the range of 154-230°C, the emissions of NO_x can be reduced to extremely low levels. Likewise, by use of fuels meeting the low sulfur parameters set forth hereinabove and additionally having a 90% boiling point (ASTM D-86) in the range of 260-320°C, particulate emissions tend to be reduced to especially low levels. To illustrate, a Detroit Diesel Corporation Series 60 Engine in the 11.1 liter configuration and nominally rated at 320 hp at 1800 rpm was used in a series of emission tests. The engine was installed in a heavy-duty transient emission cell equipped with a constant volume sampler (CVS) system. A dilution tunnel permitted measurements of HC, CO, NO_x and particulates according to the EPA Transient Emissions Cycle Procedure.

For each individual test case, the engine was started and warmed up. It was then run for 20 minutes at rated speed and load. Rated power was validated. In addition, a power test was conducted, mapping engine torque vs. speed. These parameters are required as part of the EPA Transient Cycle Procedure. Once this information was obtained, two 20-minute EPA Transient Cycles were run and engine controls were adjusted to meet statistical operating limits prescribed for the tests. The engine was shut down and allowed to soak for 20 minutes. At the end of the soak period, the Hot Start EPA Transient Cycle was run to measure NO_x, CO and particulate emissions. A second emissions evaluation was conducted after another two-minute soak. Results for the two Hot Transient Cycles were averaged into a final reported value. Whenever a fuel was changed, new fuel was introduced into the fueling system, new fuel filters were installed, and fuel lines were flushed.

Each fuel (A through D) was evaluated by the same Hot Start EPA Transient Emissions Cycle Procedure. Fuels A, B, and C contained 2-ethylhexyl nitrate in an amount sufficient to raise the cetane number of the respective fuels to a nominal value of 50. Fuel D which had a natural cetane number of 49.8 was used unaditized.

Physical and chemical characterization data for unaditized fuels A through D are shown in the following table:

TABLE

Fuel Property	A	B	C	D
Hydrocarbon Composition, vol %				
Aromatics	36.5	28.5	37.6	39.4

Continuation of the Table on the next page

TABLE (continued)

	Fuel Property	A	B	C	D
	Olefins	1.2	1.1	2.2	2.9
5	Saturates	62.3	70.4	60.2	57.7
	Carbon, wt%	86.35	86.49	86.12	87.32
	Hydrogen, wt%	13.15	13.25	12.89	13.35
10	Nitrogen, ppm	5.3	285	356	152
	Sulfur, ppm	<1	225	219	476
	Aniline pt., deg. C	70.1	60.0	65.4	69.4
15	Diene content, wt%	<0.1	0.2	<0.1	<0.1
	Viscosity, cSt				
	@ 40 deg. C	2.99	2.20	3.10	3.53
	@ 100 deg. C	1.22	0.97	1.23	1.34
20	Heat of combustion BTU/lb(kJ/g)	19,593 (45.6)	19,840 (46.1)	19,543 (45.5)	19,672 (45.8)
	Boiling range, deg. C				
	IBP	170	172	202	218
25	10%	217	211	234	252
	20%	233	222	246	262
	30%	249	230	257	271
	40%	262	237	267	278
30	50%	274	244	276	284
	60%	288	253	286	291
	70%	300	263	294	298
	80%	314	276	306	306
	90%	331	297	322	317
35	95%	344	319	338	329
	FBP	352	334	353	341
	Recovery, %	98.7	98.9	98.6	98.9
	Gravity, deg. API	34.9	36.1	34.6	34.5
40	Specific gravity	0.850	0.844	0.852	0.852
	Calculated cetane index	48.1	44.0	48.9	51.7
	Cetane index	48.5	43.8	48.3	49.7
45	Cetane number	45.3	39.6	47.7	49.8

In the above table, the following test methods were used:

- Hydrocarbon composition - ASTM D-1319
- Carbon - Carlo-Erba 1106
- Hydrogen - Carlo-Erba 1106
- Nitrogen - ASTM D-4629
- Sulfur - ASTM D-3120
- Aniline pt. - ASTM D-611
- Diene content - UOP 326
- Viscosity - ASTM D-445
- Heat of combustion - ASTM D-2382
- Boiling range - ASTM D-86

Gravity - ASTM D-287
 Calculated cetane index - ASTM D-4737
 Cetane index - ASTM D-976
 Cetane number - ASTM D 613

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Fig. 1 presents graphically the results of NO_x emissions in relation to the 10% boiling temperatures of the four fuels. It can be seen that the fuels in which the 10% boiling temperature was below 230°C had the lowest NO_x emissions.

The results of the particulate determinations are graphically depicted in Fig. 2. In this case, the results are shown as a function of 90% boiling temperatures of the base fuels. A trend toward lower particulate emissions with fuels having

10 90% boiling points within the range of $260\text{--}320^\circ\text{C}$ was noted.

Methods for reducing the sulfur content of hydrocarbonaceous middle distillate fuels or their precursors are reported in the literature and are otherwise available to those skilled in the art. Among such processes are solvent extraction using such agents as sulfur dioxide or furfural, sulfuric acid treatment, and hydrodesulfurization processes. Of these, hydrodesulfurization is generally preferred, and includes a number of specific methods and operating conditions as

15 applied to various feedstocks. For example, hydrotreating or hydroprocessing of naphthas or gas oils is generally conducted under mild or moderate severity conditions. On the other hand, sulfur removal by hydrocracking as applied to distillate stocks is usually conducted under more severe operating conditions. Vacuum distillation of bottoms from atmospheric distillations is still another method for controlling or reducing sulfur content of hydrocarbon stocks used in the production of hydrocarbonaceous middle distillate fuels. Further information concerning such processes appears in

20 Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Interscience Publishers, Volume 11, pages 432-445 (copyright 1966) and references cited therein; Idem., Volume 15, pages 1-77 and references cited therein; and Kirk-Othmer, Encyclopedia of Chemical Technology, Volume 17, Third Edition, Wiley-Interscience, pages 183-256 (copyright 1982) and references cited therein. All of such publications and cited references are incorporated herein by reference in respect of processes or methods for control of reduction of sulfur content in hydrocarbonaceous middle

25 distillate fuels or their precursor stocks.

Another method which can be used involves treatment of the hydrocarbonaceous middle distillate fuel with a metallic desulfurization agent such as metallic sodium, or mixtures of sodium and calcium metals.

Other similar embodiments of this invention will readily occur to those skilled in the art from a consideration of the foregoing disclosure.

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Claims

1. The use of a fuel-soluble combustion improver consisting essentially of 2-ethylhexyl nitrate incorporated in a hydrocarbonaceous middle distillate fuel, said fuel having the following distillation profile:

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	$^\circ\text{C}$
IBP	121-260
10%	154-288
50%	177-316
90%	204-371
EP	232-399

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- 45 and having a sulfur content of less than 500 ppm, prior to combustion in a proportion of 1000 to 5000 parts by weight per million parts of fuel for reducing emissions of at least two of NO_x , CO and unburned hydrocarbons during combustion of said fuel in a diesel engine in the presence of air.

2. The use of claim 1, wherein the base fuel has a sulfur content of 100 ppm or less and a clear cetane number in the range of 30 to 60.

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3. The use of claim 1, wherein the base fuel has a sulfur content of no more than 60 ppm.

4. The use of claim 3, wherein the base fuel has a clear cetane number in the range of 50 to 60.

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5. The use of claim 3, wherein the base fuel has a clear cetane number in the range of 40 to 50.

6. The use of any one of the preceding claims, wherein emissions of NO_x , CO and unburned hydrocarbons are reduced.
7. The use of any one of the preceding claims, wherein the base fuel has a 10% boiling point (ASTM D-86) in the range of 154-230°C.
8. The use of any one of the preceding claims, wherein the base fuel has a 90% boiling point (ASTM D-86) in the range of 260-320°C.

10 Patentansprüche

1. Verwendung eines in Treibstoff löslichen Mittels zur Verbesserung der Verbrennung, das im wesentlichen aus in einen Mitteldestillat-treibstoff aus Kohlenwasserstoffen eingearbeitetem 2-Ethylhexylnitrat besteht, wobei der Treibstoff das folgende Destillationsprofil:

	°C
IBP	121-260
10%	154-288
50%	177-316
90%	204-371
EP	232-399

und einen Schwefelgehalt von weniger als 500 ppm, vor der Verbrennung in einer Menge von 1000 bis 5000 Gewichtsanteilen auf eine Million Teile Treibstoff aufweist, um die Emissionen von mindestens zwei aus der Reihe NO_x , CO und nichtverbrannten Kohlenwasserstoffen während der Verbrennung des Treibstoffs in einem Dieselmotor in Anwesenheit von Luft zu verringern.

2. Verwendung gemäß Anspruch 1, bei der der Grundtreibstoff einen Schwefelgehalt von 100 ppm oder weniger und eine reine Cetanzahl im Bereich von 30 bis 60 aufweist.
3. Verwendung gemäß Anspruch 1, bei der der Grundtreibstoff einen Schwefelgehalt unterhalb von 60 ppm aufweist.
4. Verwendung gemäß Anspruch 3, bei der der Grundtreibstoff eine reine Cetanzahl im Bereich von 50 bis 60 hat.
5. Verwendung gemäß Anspruch 3, bei der der Grundtreibstoff eine reine Cetanzahl im Bereich von 40 bis 50 hat.
6. Verwendung gemäß einem der vorstehenden Ansprüche, bei der die Emissionen an NO_x , CO und nichtverbrannten Kohlenwasserstoffen reduziert sind.
7. Verwendung gemäß einem der vorstehenden Ansprüche, bei der der Grundtreibstoff einen 10 %igen Siedepunkt (ASTM D-86) im Bereich von 154 - 230°C hat.
8. Verwendung gemäß einem der vorstehenden Ansprüche, bei der der Grundtreibstoff einen 90 %igen Siedepunkt (ASTM D-86) im Bereich von 260 - 320 °C hat.

Revendications

1. Utilisation d'un agent améliorant la combustion, soluble dans les carburants, consistant essentiellement en nitrate de 2-éthylhexyle incorporé à un carburant consistant en un distillat moyen hydrocarboné, ledit carburant ayant le profil de distillation suivant :

	°C
IBP	121-260

Suite du Tableau sur la page suivante

(suite)

	°C
10%	154-288
50%	177-316
90%	204-371
EP	232-399

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10 et ayant une teneur en soufre inférieure à 500 ppm, avant combustion, en une proportion de 1000 à 5000 parties en poids par million de parties de carburant pour réduire les émissions d'au moins deux des composés consistant en NO_x , CO et hydrocarbures imbrûlés au cours de la combustion dudit carburant dans un moteur diesel en présence d'air.

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2. Utilisation suivant la revendication 1, dans laquelle le carburant de base a une teneur en soufre égale ou inférieure à 100 ppm et un indice de cétane clair compris dans l'intervalle de 30 à 60.

3. Utilisation suivant la revendication 1, dans laquelle le carburant de base a une teneur en soufre non supérieure à 60 ppm.

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4. Utilisation suivant la revendication 3, dans laquelle le carburant de base a un indice de cétane clair compris dans l'intervalle de 50 à 60.

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5. Utilisation suivant la revendication 3, dans laquelle le carburant de base a un indice de cétane clair compris dans l'intervalle de 40 à 50.

6. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle les émissions de NO_x , de CO et d'hydrocarbures imbrûlés sont réduites.

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7. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le carburant de base a un point d'ébullition à 10 % (ASTM D-86) compris dans l'intervalle de 154 à 230°C.

8. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le carburant de base a un point d'ébullition à 90 % (ASTM D-86) compris dans l'intervalle de 260 à 320°C.

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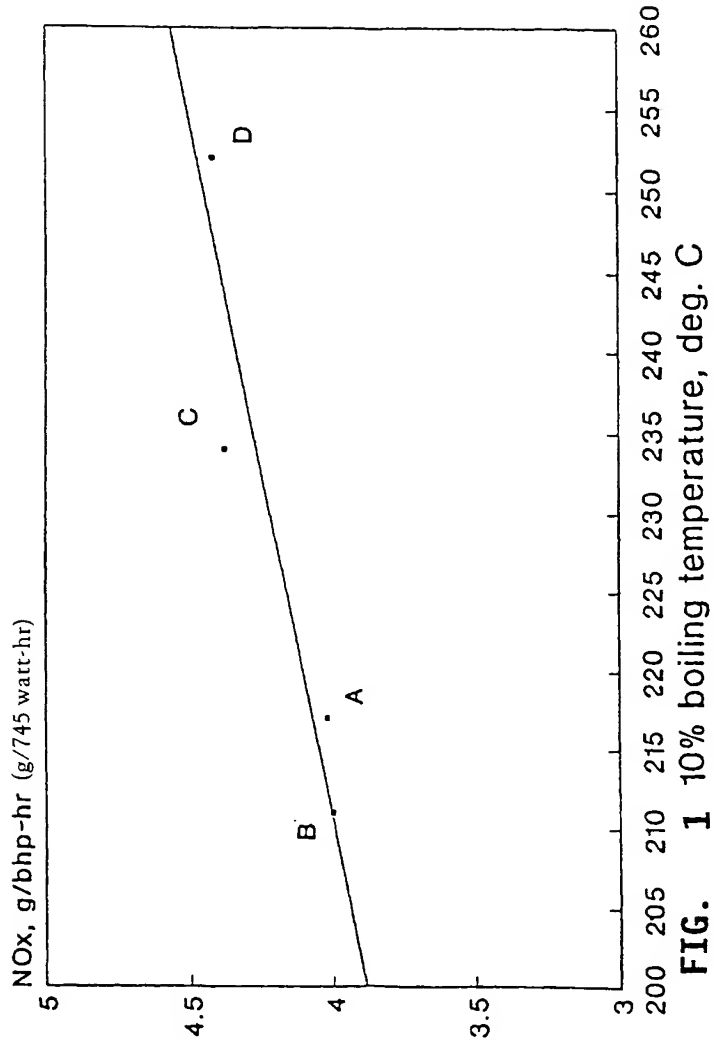


FIG. 1 10% boiling temperature, deg. C

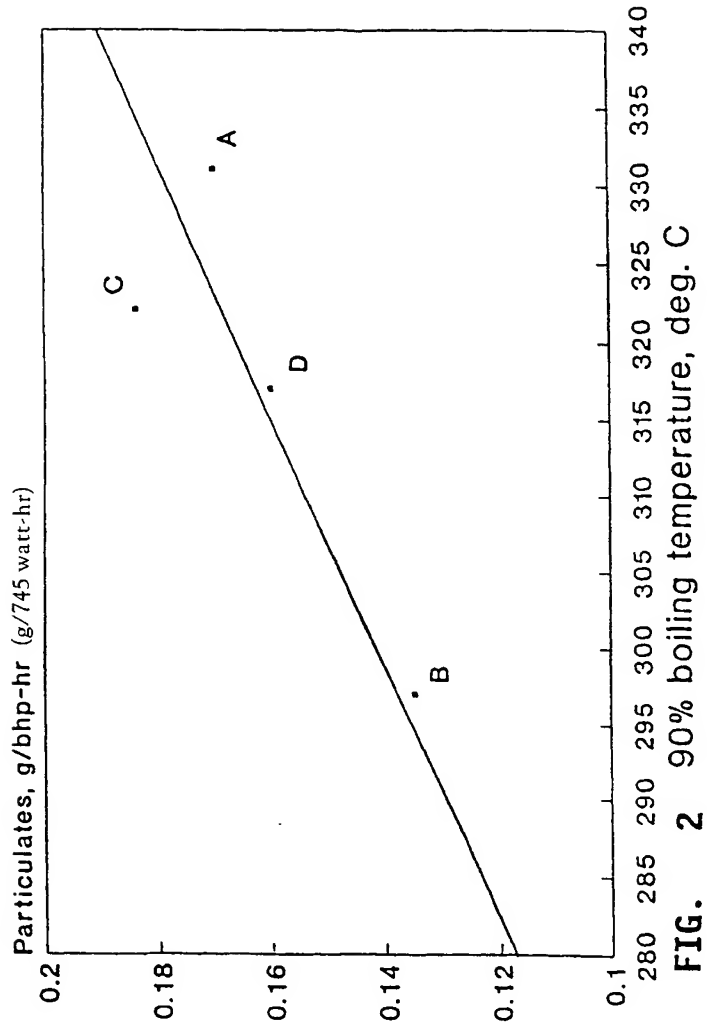


FIG. 2 90% boiling temperature, deg. C